EUTROPHICATION CONTROL

Nutrient Inactivation by Chemical Precipitation at Horseshoe Lake, Wisconsin

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ABSTRACT

Numerous methods have been suggested for retarding or reversing lake eutrophication, a process that occurs under natural conditions but is sharply accelerated by activities of man. Nutrient inactivation by chemical means is one method that has been proposed. The method reported here seeks to limit nuisance algal production resulting from lake fertilization by the use of alum (aluminum sulfate) to remove phosphorus, one critical element for plant nutrition. The method represents an extrapolation of advanced waste treatment technology to a natural lake setting where phosphorus is removed by precipitation, sorption, and physical entrapment and sedimentation in a flocculant aluminum hydroxide precipitate. Prior to the effort by the Inland Lake Demonstration Project, this method had never been tried before in the United States on an entire lake.

Horseshoe Lake, a 22-acre (8.9 ha), 55-foot (16.7 m) deep, eutrophic lake in east central Wisconsin was treated in May, 1970, when approximately 11 short tons of slurried alum were distributed in its upper 2 feet of water. Alum concentrations in the treated volume were about 200 mg/l (18 mg Al/l), which, based on laboratory testing, resulted in maximum phosphorus removal with minimal ecologic risk. The results of the treatment include: (1) a decrease in total phosphorus in the lake; (2) no large increase in total phosphorus in the anoxic hypolimnion during summer stratifications following treatment as noted in other eutrophic lakes and prior to treatment in Horseshoe Lake; (3) some increase in the transparency of the water during the summer following treatment; (4) a short-term decrease in color; (5) an absence of the nuisance planktonic algal blooms that had been common in previous years; (6) an improvement in dissolved oxygen conditions, especially during the following two winters; and (7) no observations of adverse ecological consequences.

The generally positive results obtained in this demonstration project will hopefully stimulate longer-term and more thorough research evaluations of this potentially fruitful renovation technique for eutrophic lakes.

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INTRODUCTION

The many thousands of lakes in the Upper Great Lakes region comprise a valuable natural resource that is showing signs of deterioration due to use and abuse by ever-increasing numbers of people. Because these lakes form the base of the recreation/tourist-oriented economy of the region, there has been strong public interest in and demand for water quality maintenance and improvement. The Inland Lake Renewal and Management Demonstration Project is one attempt to respond to this need. An action program by design, the Project is a joint venture of the Wisconsin Department of Natural Resources and the University of Wisconsin, and is sponsored by the Upper Great Lakes Regional Commission, a federal economic development agency.

From its inception in May, 1968, broad objectives of the Inland Lake Project have been the demonstration of techniques to restore, maintain, and protect a high quality environment in lakes and on their adjacent shorelands. Degradation of many of the lakes in the region is the result of accelerated lake eutrophication largely attributable to the activities of man. The in-lake renewal phase of the Lake Demonstration Project is attempting to show, by example, how to restore eutrophic lakes. Numerous methods have been suggested for retarding or reversing lake eutrophication (Stewart and Rohlich, 1967; Greeson, 1969; National Academy of Sciences, 1969). Nutrient inactivation by chemical means is one of those that have been proposed. The effectiveness of aluminum as a precipitating agent for phosphorus has been demonstrated in the laboratory, and applied in industrial processing as well as in municipal sewage and water treatment plants. The removal of a critical element for plant nutrition (phosphorus) from a natural lake system appeared promising. Orthophosphate in the lake water could be precipitated or sorbed, by an ion or hydroxide of aluminum, after application of an aluminum salt to the lake. Particulate phosphorus could also be removed by entrapment and subsequent sedimentation in the flocculant aluminum hydroxide matrix. The immediate effects on dissolved organic phosphorus would be minimal.

This potential nutrient inactivation method had never been used before on a full-scale basis in North America. Three Swedish lakes have been treated with aluminum sulfate since 1968 (Jernelov and Lundstrom, 1969; Jernelov, 1970; Malueg, 1972.) A short-term decrease in total phosphorus concentration and improvement in dissolved oxygen conditions have been reported for Langsjön (Landner, 1970).

The use of such a method for limiting planktonic plant and algal growth in a Wisconsin lake has been investigated in this portion of the Inland Lake Demonstration Project. Specific goals were to: (1) demonstrate that suitable techniques can be devised for the safe and effective application of the chemical, (2) document the effects of the precipitating agent on the water chemistry and algal community of the lake, and (3) determine the costs of application and the benefits or improvements that may accrue. The potentially rapid response to treatment and the possible widespread applicability of the method were the bases for undertaking a demonstration and evaluation of the technique. This report documents our experiences and results to date.

SITE SELECTION

The criteria for choosing a demonstration site were:

(1) The lake should be classified as eutrophic or mesotrophic. Nutrient concentrations should be present at sufficient levels to allow detection of change.

(2) Background data should be available on the chemical and physical characteristics of the lake.

(3) The surface area should be large enough to allow its characterization as a typical lake, but small enough to permit treatment and monitoring within the budgetary limits of the project; preferably between 10 and 50 acres (4-20 ha).

(4) Depth should be great enough to allow the formation of a persistent thermocline and a well-defined hypolimnion so that the precipitate may settle with minimum interference subsequent to treatment.

(5) The lake should have public access.

(6) The retention time of water within the basin should be long enough to prevent the effects of rapid water exchange from masking the consequences of the treatment.

(7) The nutrient input from the watershed should be minimal. Surface drainage, agricultural runoff and other sources must not overshadow the effects of the demonstration. The watershed should be small and the number of tributaries limited in order to minimize outside contributions.

Horseshoe Lake in east central Wisconsin largely satisfied the site selection criteria, and was chosen as the demonstration site. It is 22 acres (8.9 ha) in area, eutrophic, accessible, dimictic, and had been monitored for one year in 1966. Although the nutrient budget for the lake was unknown, there were no obvious existing point sources of nutrient input to the lake. The inlet and outlet streams were listed as intermittent waterways; therefore, the mean retention time of water in the lake was assumed to be long enough so as not to obscure the results of chemical treatment. Given the relatively short duration of this lake renewal activity, the most important criterion for site selection was the availability of background information.

DESCRIPTION

GENERAL SETTING

Horseshoe Lake is located in Section 20, T17N, R22E, Manitowoc County, Wisconsin (Fig. 1). It has a surface area of 22 acres (8.9 ha), a maximum depth of 55 feet (16.7 m), and lies in a drainage basin of about 1,700 acres (700 ha) as shown in Figures 1 and 2. The area/volume/depth relationships for the lake are presented on Figure 3.

The hilly and irregular topography and the surficial deposits of the drainage basin are a product of late Pleistocene glaciation. The area has approximately 80 feet (24.4 m) of topographic relief. Glacial drift in the area is about 125 feet (38.1 m) thick and is composed largely of sandy and calcareous clay (Ostrom, 1970). The glacial deposits are underlain by Niagara dolomite. Soils developed on the glacial deposits include silt loams and silty clay loams mixed with limestone and shale, generally assigned to the Kewaunee soils series.

Shoreland trees are principally white cedar and birch. Farther back from the shoreline stand oak, elm, maple and a few white pine. A variety of shrubs and wild grasses, as well as sparse stands of cattails, occupy the lake edge.

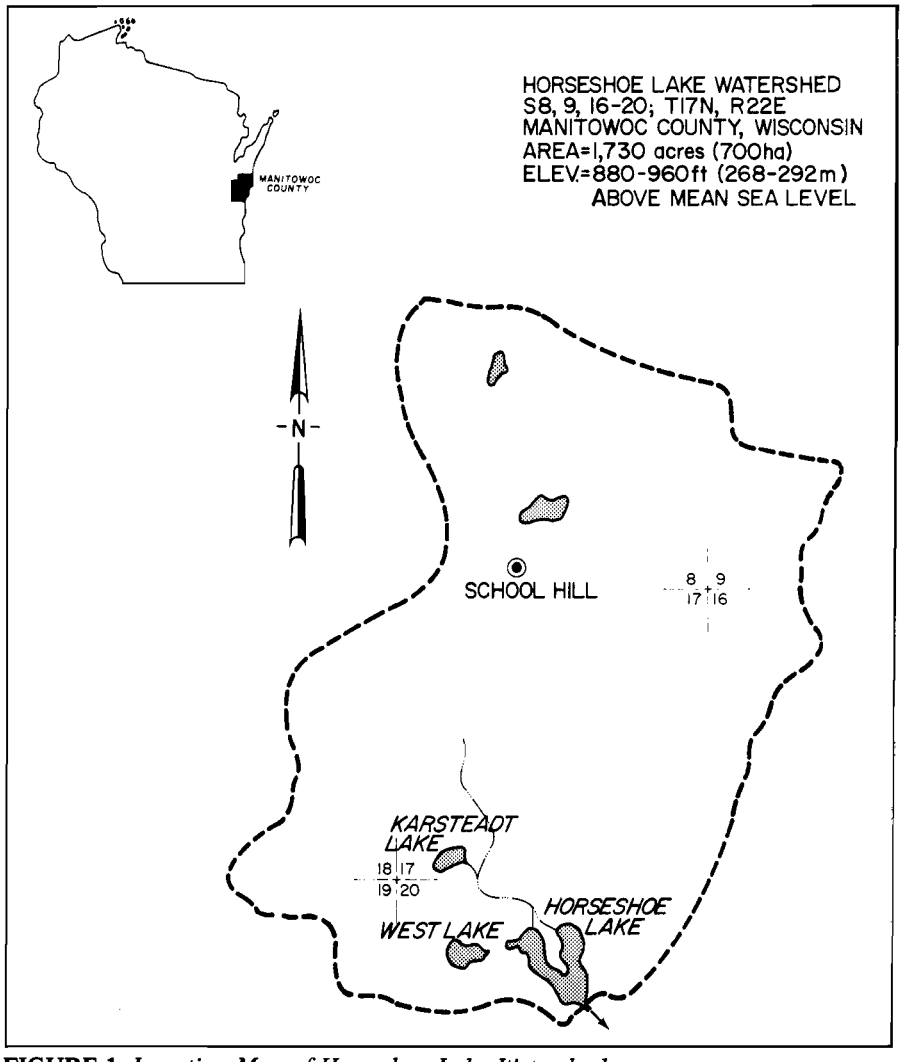


FIGURE 1. *Location Map of Horseshoe Lake Watershed.*

CLIMATE

This part of Wisconsin has a mean annual temperature of 47F (8.3C) and a mean annual precipitation of about 30 inches (76 cm) (Table 1). Monthly precipitation data are shown on Figure 4. The prevailing winds are westerly, but storms and high winds occasionally arise from northeast and southeast.

TABLE 1. Annual Precipitation at the Chilton Sewage Treatment Plant*

Year	Rainfall (inches)	Year	Rainfall (inches)
1960	31.77	1966	29.60
1961	31.82	1967	32.55
1962	27.92	1968	26.73
1963	23.66	1969	30.82
1964	30.09	1970	31.03
1965	39.56	1971	38.94

*Data were obtained from the U. S. Weather Bureau Station at Chilton, located about 15 miles (24 km) northwest of Horseshoe Lake.

HYDROLOGY

Although only minimal hydrologic and hydrogeologic investigations of the Horseshoe Lake basin were conducted, estimates of the rates and volumes of water movement through the lake provide an indication of retention time for lake waters. The Horseshoe Lake drainage basin is difficult to define, but it is no larger than 1,730 acres (700 ha) in area. Based on a 0.25 runoff coefficient for the 30 inches (76 cm) of annual precipitation, runoff amounts to about 1,050 acre-feet (1.3×10^6 cu m) annually. The volume of Horseshoe Lake is 375 acre-feet (3.6×10^5 cu m); retention time for Horseshoe Lake under these assumptions is about 0.35 years. This probably represents a minimum retention time.

Personal observations of outlet water stage, made both by the area fish manager and a riparian property owner over the past ten years, confirm that outlet flow has been intermittent during the year, and that maximum discharge occurs during spring runoff.

The spring maximum and intermittent nature of lake outlet flows has

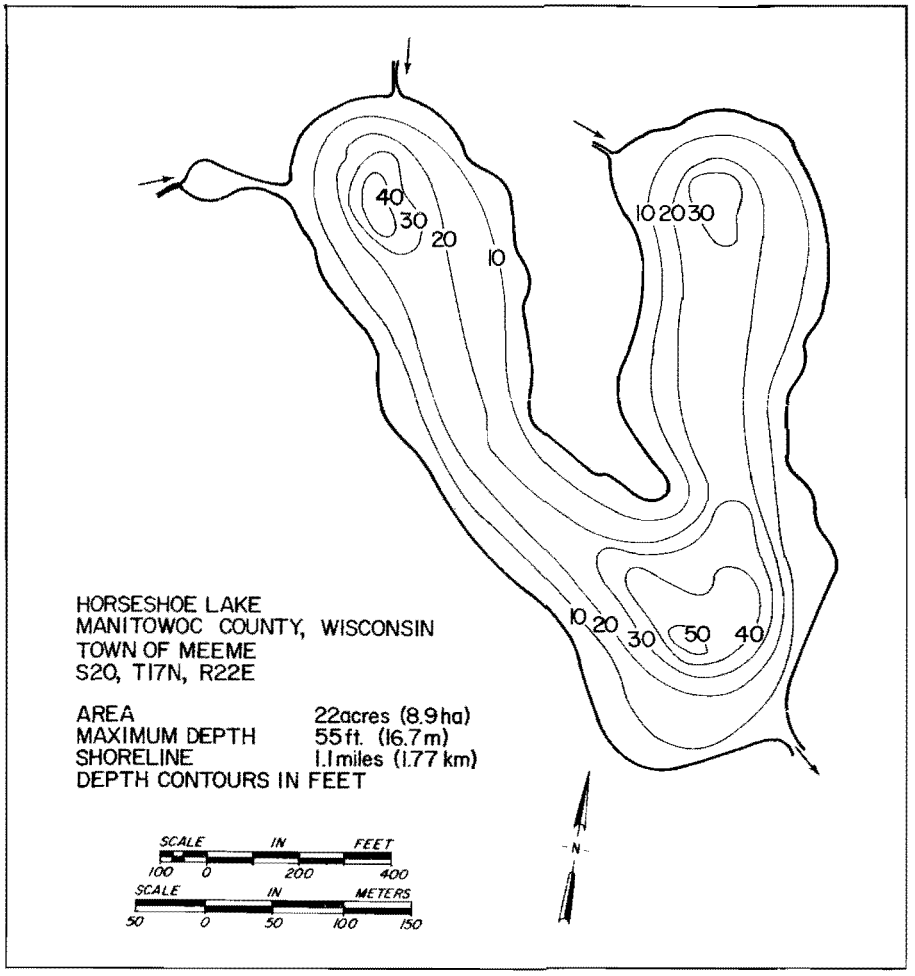


FIGURE 2. *Bathymetric Map of Horseshoe Lake.*

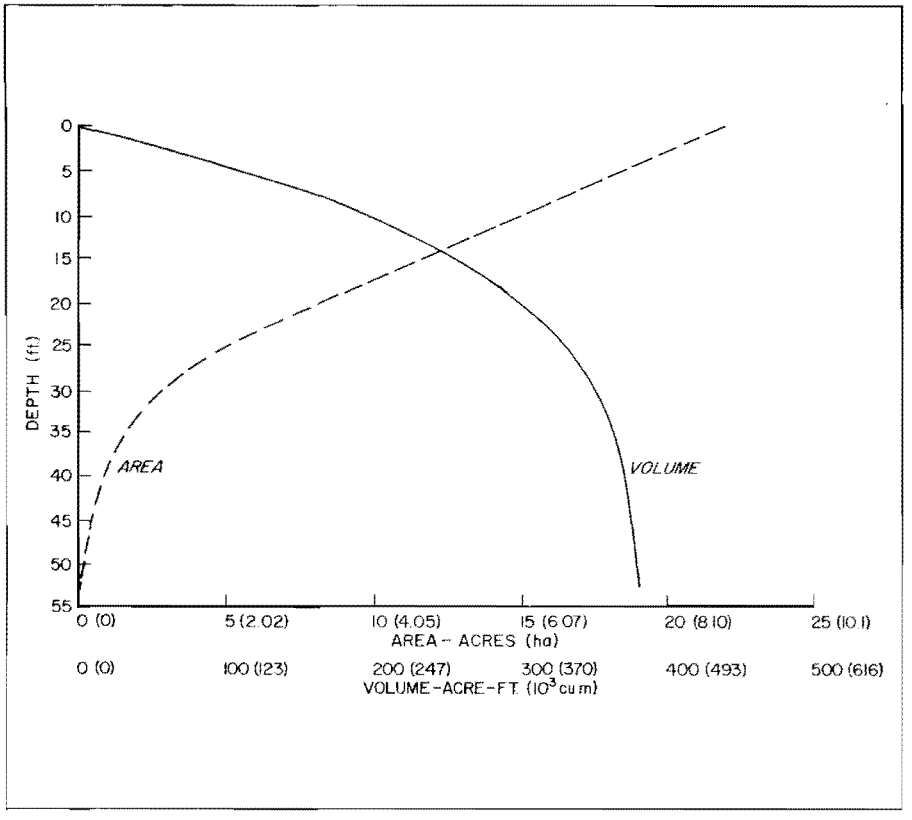


FIGURE 3. *Area-Volume-Depth Relations for Horseshoe Lake.*

been substantiated by data from 1971. Figure 5 shows estimates of precipitation for the lake area and discharge measurements made at the lake outlet during 1971. Assuming that the discharge measurements represent points on a smooth hydrographic curve for the year, integration of the discharge–time curve results in an estimated 550 acre-feet of surface water moving out of Horseshoe Lake in a year. This volume would be equivalent to a mean residence time of water in the lake of about 0.7 years. This is the best estimate of mean residence time currently available for the lake, and is calculated based on a year which had 8 inches of precipitation above the average.

Because treatment of Horseshoe Lake was scheduled after spring runoff, flushing of water through the lake would not markedly obscure the short-term results of treatment.

A survey was made in September, 1971 to determine the chemical composition of groundwater in the Horseshoe Lake area. Analyses of samples from six nearby wells (Table 2), four of which are up-gradient from the lake, showed that the well waters were of high quality (low nutrient content) and suggest that groundwater inflows to the lake would not contribute high concentrations of phosphorus.

LIMNOLOGY

Limnologically, Horseshoe Lake has characteristics common to many deep eutrophic lakes in the Upper Great Lakes region. It is a slightly colored, hard-water lake which develops a persistent thermocline during the warm months at depths of 12-18 feet (3.7-5.5 m). The hypolimnion has exhibited rapid depletion of dissolved oxygen and the production of anaerobic by-products such as sulfides and ammonia. Although thermal profiles indicate that the lake is dimictic, the degree of mixing and consequent re-aeration appears to be limited by the sheltered nature of the basin. The tree-covered hills and ridges surrounding the lake allow only strong northerly or southerly winds to have any pronounced mixing effect. Because of incomplete re-aeration and/or a high rate of oxygen demand, dissolved oxygen has been depleted soon after the formation of ice cover. The navigable inlet from West Lake and spring sources arising in the terminal moraines apparently provide

some oxygenated water throughout the winter, permitting a marginal carryover of the present fish population.

Prior to treatment, the lake was eutrophic, as indicated by analytical nitrogen and phosphorus values as well as by seasonal depletion of dissolved oxygen and excessive algal growths. The general range of physiochemical background data is shown in Table 3. While agricultural drainage and natural runoff undoubtedly contribute to nutrient input, a suspected past point source of nutrients was a cheese and butter factory located at School Hill, north of the lake (Fig. 1). This plant had been in operation for several decades before closing in April, 1965. In early 1963, tiles were installed which allowed direct drainage from the company's waste lagoon to the northern inlet of the lake.

Prior to installation of the tile system at the cheese and butter factory, Horseshoe Lake had a sport fishery consisting of largemouth bass *(Micropterus salmoides)* and panfish; since 1957, the lake had also been successfully managed for brown *(Salmo trutta)* and rainbow trout *(Salmo gairdneri)*. During the winters of 1964, 1965 and 1966, extensive fish kills attributed to suffocation were documented at Horseshoe Lake (information on file with the Wisconsin Department of Natural Resources). Dissolved oxygen data are lacking for the period 1967-69, but in 1970 winter dissolved oxygen concentrations were near zero in the vertical profiles analyzed.

The area fish manager and a local resident have stated independently that prior to 1962-63, there were no nuisance plant growths at Horseshoe Lake (although some incipient problems were noted in 1962). For 1963 to 1969, nuisance blooms of blue-green algae occurred. The severity of the algal problem was reported to be roughly proportional to the amount of copper sulfate which was used for its control (Table 4).

The littoral zone has been nearly a continuous band of *Myriophyllum spicatum* (water milfoil), a recent Eurasian invader, which has also caused serious problems in a few other southern Wisconsin lakes. Abundant growths of *Chara* have been common in recent years. The bottom of Horseshoe Lake slopes steeply downward and the littoral zone is, therefore, fairly narrow. Rooted plants rarely extend more than about 30 feet

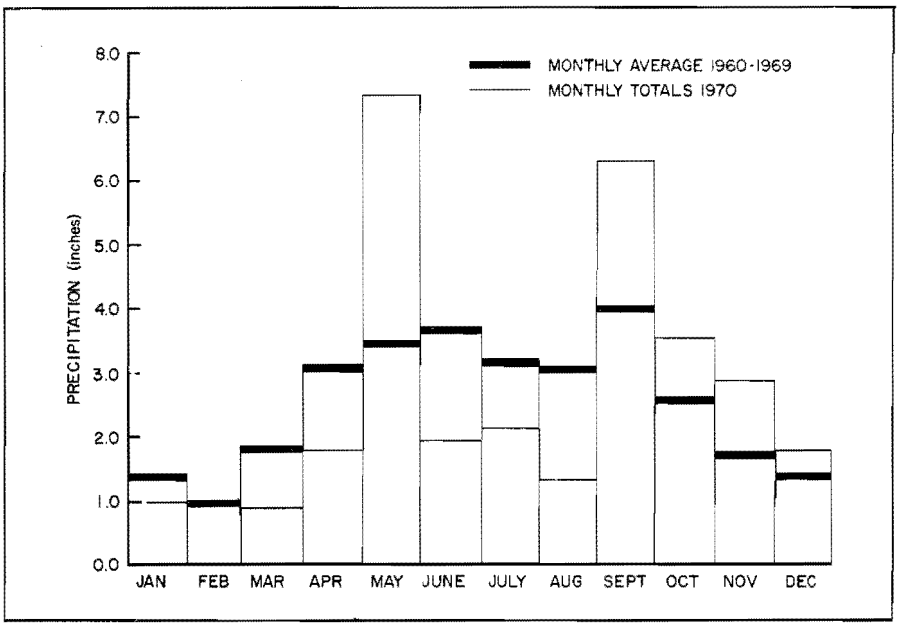


FIGURE 4. *Monthly Precipitation Data for Horseshoe Lake Area. (Total Precipitation, Chilton Sewage Treatment Plant; average annual ppt. 1960-69: 30.5 inches.)*

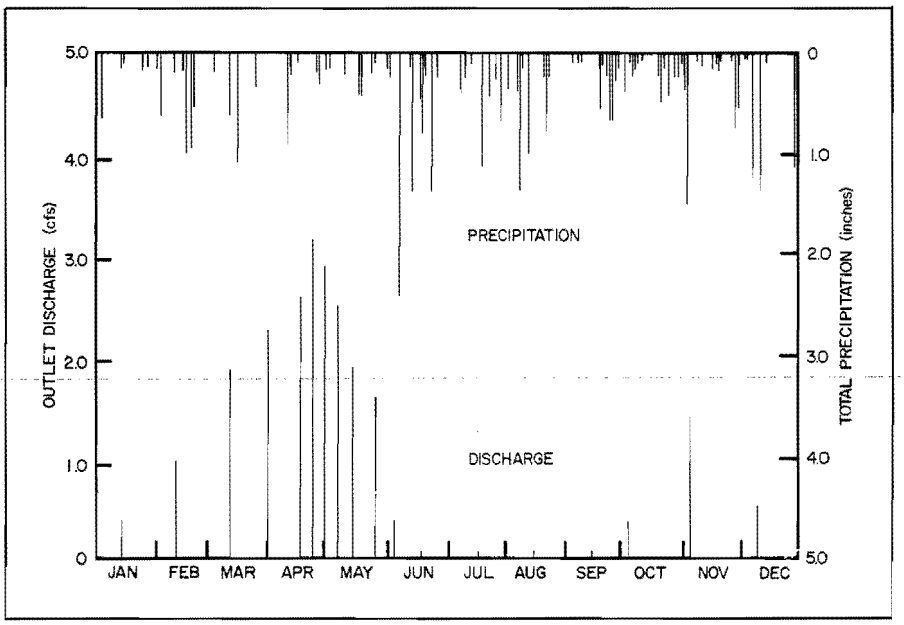


FIGURE 5. *Precipitation and Lake Outlet Discharge, Horseshoe Lake, 1971.*

(10 m) horizontally out from shore. Nevertheless, attached aquatic plants are regarded as a nuisance and local riparians have requested advice on control measures for areas in which swimming and boating have been impaired. Table 5 presents a list of rooted aquatic plant species found in Horseshoe Lake. As the growing season progresses many of the plant species become encrusted with calcium carbonate.

Observations of the planktonic algae during the period from 1963 to 1969 cite prominent blooms of *Anabaena*, *Microcystis*, and *Oscillatoria*. In addition to these, a variety of copepods, cladocerans, flagellates and rotifers contribute to the community structure. Large populations of *Daphnia* and *Chaoborus* have been observed. An examination of an ice profile in March, 1970, showed three distinct pink colored bands that contained *Oscillatoria rubescens*, indicating that algal blooms had occurred under ice cover.

The lake contains three sub-basins separated by low, narrow saddles. Bottom sediments are primarily muck and

TABLE 2. Ground Water Quality Near Horseshoe Lake*

Parameter	Measurement
NO_3^-–N	0.06–2.0 mg/l
Total N	0.1–2.1 mg/l
Reactive P	<0.01–0.01 mg/l
Total P	<0.02–0.04 mg/l
Calcium	43–47 mg/l
Sodium	2–4 mg/l
Chloride	2–6 mg/l
Well depths	10–60 feet below land surface

*Range of values from 6 wells, 4 north of the lake and 2 south of the lake; all within ½ mile radius of lake.

TABLE 3. Range of Physiochemical Data for Horseshoe Lake*

Parameter	Epilimnion	Hypolimnion
Temp. in °F	32–78	32–48
D. O. in mg/l	< 0.5–14.3**	0–4.3
pH	7.2–8.9	6.8–8.3
Total Alkalinity (mg $CaCO_3$/l)	218–252	220–278
Total Hardness (mg $CaCO_3$/l)	254–300	276–306
Nitrite–N in mg/l	0.004–0.089	0.002–0.213
Nitrate–N in mg/l	0.10–0.90	0.10–0.76
Ammonia–N in mg/l	0.06–1.96	0.16–6.33
Organic N in mg/l	0.76–2.19	0.75–1.68
Diss. P in mg/l	0.01–0.48	0.26–1.52
Total P in mg/l	0.05–0.50	0.31–1.54

*From files of the Wisconsin Department of Natural Resources, State Laboratory of Hygiene: data gathered from January, 1966 to April, 1967.

**Minimum oxygen value taken from field data on file with the Wisconsin Department of Natural Resources, Area Office, Plymouth (1965).

TABLE 4. Copper Sulfate Treatments at Horseshoe Lake*

Year	Amount
1965	400 lbs. (181 kg) $CuSO_4 \cdot 5H_2O$
1966	100 lbs. (45.3 kg)
1967	200 lbs. (90.6 kg)
1968	110 lbs. (49.8 kg)
1969	350 lbs. (159 kg)
1970	75 lbs. (34.1 kg)
1971	60 lbs. (27.2 kg)

*From Wisconsin Department of Natural Resources, Aquatic Nuisance Control Section. 1965–69, chemical used for planktonic and filamentous algae control; 1970, 1971 for filamentous algae (*Chara*) control.

marl, with sand and gravel in some near shore areas. The north and east shorelines and the peninsula are low-lying and peaty. The south and west shorelines rise to morainal ridges and have 13 of the 15 dwellings on the lake. The adjoining wetlands cover less than one acre.

LABORATORY STUDIES

OBJECTIVES

Laboratory studies were conducted on Horseshoe Lake water to help provide information regarding: (1) the selection of treatment materials and dosages required for good floc formation and phosphorus removal, (2) alternative application methods, and (3) some of the possible effects that treatment might have on the ecology of the lake.

MATERIALS SELECTION

Review of the literature indicated that aluminum(III) would meet the criteria for a chemical precipitant, i.e., (a) effective removal of dissolved phosphorus and particulate material under conditions (of pH, dissolved solids, etc.) that are common to lake waters, (b) low toxicity to many forms of life, and (c) relatively low cost. Epilimnetic water samples were obtained in several 5-gallon (20 l) carboys from the ice-covered lake in March, 1970, for laboratory studies. Dissolved-reactive and total phosphorus concentrations of the water were 0.09 and 0.17 mg/l, respectively.

Jar tests were run (using 0.26 gal (1.0 l) water samples in 1.5-liter beakers on a six-place, Phipps and Bird, variable-speed paddle mixer) to determine suitable dosages. A 30-second rapid mix, followed by 10 minutes of gentle mixing, was used in the jar test procedure. Settling times of 1, 6 and 24 hours were allowed for determination of total phosphorus removals in the beakers. The initial tests were conducted at 39 F (4C).

Commercial standard ground aluminum sulfate ($Al_2(SO_4)_3 \cdot 14H_2O$) and sodium aluminate ($Na_2O \cdot Al_2O_3 \cdot 3H_2O$) were considered as sources of aluminum, but alum (aluminum sulfate) was subsequently chosen based

TABLE 5. Rooted Aquatic Plants Present in Horseshoe Lake, July, 1971

Heteranthera dubia	water star grass
Myriophyllum spicatum	Eurasian water milfoil
Nuphar variegatum	yellow water lily
Nymphaea tuberosa	white water lily
Potamogeton natans	floating-leaf pondweed
P. nodosus	American pondweed
P. pectinatus	Sago pondweed
P. richardsoni	Richardson's pondweed

on its effectiveness and total cost. Aluminum dosages up to 27 mg/l were tested. About 7 mg Al/l were required to form a visible floc, but about 14 mg/l were required to produce a good settleable floc. Maximum total phosphorus removals of 71 percent were obtained using 20 mg Al/l (after settling times of one hour). Dissolved phosphorus (as determined by analyzing the filtrate from a 0.45 µm membrane filter) was reduced by 97 percent in all beakers which formed a floc. Jar test data are shown in Table 6.

The use of several coagulant aids with alum was considered. Trials confirmed that the addition of some anionic and cationic polyelectrolytes added simultaneously with the aluminum had no positive effect on phosphorus removal. (Two-step treatment of the lake was not considered feasible). A possible adverse effect was noted, however; the polyelectrolytes formed a more cohesive floc, which increased its tendency to retain gas bubbles and to float. Bentonite, Fuller's earth, and fly ash were also applied with alum as weighting agents, but no enhancement of phosphorus removal was noted at economic levels.

METHOD OF APPLICATION

In order to develop criteria for a method of application, experiments were run to determine the characteristics of floc formation using ground alum as opposed to an alum slurry. Jar tests had shown that equivalent amounts of alum produced comparable results if several minutes of rapid mixing time were allowed for the ground alum to dissolve. To apply these results to a system which would more closely resemble lake conditions, a 10-foot-tall (3 m) column of 3.5 inches (8.9 cm) I.D. acrylic resin was filled with 3.96 gal (15 l) of lake water. Portions of dry and slurried alum were mixed into the surface 1 foot (30 cm) of the water column; this upper zone had been partially isolated from the lower waters by a perforated baffle. After several seconds of mixing, the baffle was removed and the chemicals were allowed to settle. Visual observations indicated that a poor floc was formed using the dry alum, and substantial portions of the material settled directly to the bottom of the column. Addition of 18 and 22 mg of Al/l (as a slurry of alum) to the top foot of the water column resulted in 88 percent and 30 percent removal of dissolved and total phosphorus, respectively, throughout the column, after a settling period of six hours. Several days were required before the quiescent water column cleared. Because the phosphorus remaining in aluminum-treated water was primarily particulate material, total phosphorus removal increased to about 80 percent as the turbidity decreased.

It was apparent from jar tests that good mixing of the alum slurry into the lake water would be necessary in order to obtain substantial phosphorus removal. Although successful application of the chemical to the lake necessitates thorough mixing, care would be required to avoid mixing the alum throughout too large a volume of the surface waters, thereby reducing aluminum dosages to less effective levels. Based on the bench-scale testing of aluminum treatment, the plan for lake treatment included the addition of a slurry of alum to the surface 2 feet of water in the lake. This treatment method should significantly reduce color, turbidity, and total phosphrous concentrations by formation and settling of hydrous aluminum oxide floc. A treatment level of about 18 mg Al/l (200 mg alum/l) was proposed.

SECONDARY EFFECTS OF TREATMENT

Changes in pH, color and alkalinity of the lake water were observed in bench studies. Color removals were noted in the jar test studies (Table 6) as anticipated from water treatment plant experience. True color (determined by using color comparison discs on a 0.45 µm filtered sample) was reduced from an initial 25 standard color units to 5-7 units in beakers treated with 14-27 mg Al/l. Color was reduced to 10 units at an Al level of 7 mg/l. In the column tests, color reductions of about 20 percent were noted, indicating that color is more effectively removed by the forming floc, rather than by a pre-formed floc.

The pH and total alkalinity both decreased with increasing aluminum dosages, as anticipated from the relation:

$$\begin{array}{c} 3CO_2\uparrow \\ + \\ Al^{+++} + 3(OH)^- \rightleftharpoons \underline{Al(OH)_3} \\ \downarrow\uparrow \\ 3HCO_3^- \end{array}$$

The decrease in pH, limited by the high buffer capacity of Horseshoe Lake water, resulted in conditions more suitable for effective treatment by aluminum.

ECOLOGICAL IMPACTS

Literature surveys and laboratory studies were undertaken to determine the short-term ecologic consequences, if any, of the proposed alum treatment. Stresses that might be imposed on the aquatic ecosystem include: (1) the addition of aluminum, sulfate and possibly trace contaminants in the alum to the lake, (2) a short period of high turbidity following treatment, and (3) decreases in pH and alkalinity in surface waters.

Because rainbow trout had been planted in the lake previously and because this species is environmentally sensitive, laboratory experiments were conducted to ascertain the short-term effects of alum treatment at various dosages on rainbow fingerlings. Six 2-3 inch long (6-8 cm) fingerlings were placed in each of nine 4-liter (1 gal) beakers. Water temperature was maintained at about 63F (17.5C) and dissolved oxygen at about 8.5 mg/l. Both fish hatchery and Horseshoe Lake waters were used as controls. Aluminum dosages ranged from 7 to

TABLE 6. Jar Test Results for Aluminum Treatment of Horseshoe Lake Water

	Alum Dosage mg/l (mg/l Aluminum)				
	0 (0)	75 (7)	150 (14)	225 (20)	300 (27)
Phosphorus mg/l					
Dissolved	0.086	< 0.003	< 0.003	< 0.003	<0.003
Total	0.17	0.105	0.07	0.05	0.055
P Removal %*					
Total	–	38	59	71	66
Alkalinity mg/l as $CaCO_3$	246	212	–	143	112
Color Units	25	10	7	5	5
pH	8.0	7.3	7.25	7.2	7.1
Conductivity in µmhos/cm at 20°C	510	535	540	545	580
Floc	–	pinpoint	good	copious	copious

*Floc settling time of one hour.

27 mg/l, which bracketed the proposed treatment level of 18 mg Al/l.

Experimental treatments and results are summarized in Table 7. The results indicated that: (1) the pH decrease in the aerated, treated portion of the lake would be about 0.2 units, and this change apparently had no immediate effect on the fish; (2) the proposed level of treatment of 18 mg Al/l (added as alum or sodium aluminate) would have little effect on the existing or planted trout fishery; (3) the high solids concentrations associated with floc formation were detrimental to fish only at aluminum levels 50 percent higher than the proposed treatment (fish could avoid prolonged exposure to these conditions since only about 10 percent of the volume of the lake was to be treated), and (4) the *dissolved* materials associated with the alum treatment did not have an adverse short-term effect on the fingerlings (compare data on beakers No. 5 and No. 9 in Table 7).

TABLE 7. Fish Reaction Tests, Horseshoe Lake

	Beaker Number and Contents								
	1 Horseshoe Lake Water	2 Nevin Fish* Hatchery Water	3 Horseshoe Lake Water	4 Horseshoe Lake Water	5 Horseshoe Lake Water	6 Horseshoe Lake Water	7 Nevin Fish Hatchery Water	8 Horseshoe Lake Water	9 Horseshoe Lake Water
Treatment	Control	Control	Decant from Column treatment at 18 mg/l of Al added as alum	18 mg Al/l added as alum	27 mg Al/l added as sodium aluminate	7 mg Al/l added as alum	18 mg Al/l added as alum	18 mg Al/l added as sodium aluminate	Decanted liquid from number 5
pH	8.0	7.9	7.8	7.8	8.4	7.9	7.8	–	8.4
Conductivity in µmhos/cm at 20° C	475	520	480	490	520	470	535	–	520
Observations									
6 Apr 1500 hrs.	Start	Start	Start	Start	Start	Start	Start	–	–
1700					2 dead				
2100					6 dead				
2200					6 new fish		1 dead		
7 Apr 0830					6 dead, 6 new fish			Start	
1100		1 jumped out			4 dead				
1300					6 dead, STOP (Decant for trial No. 9)			1 jumped out	Start 6 new fish
8 Apr									
9 Apr									
12 Apr									
13 Apr		Stressed reactions							
17 Apr	Normal	Stressed reactions	Stressed reactions	Normal	–	Normal	Normal	Normal	Normal

*Wisconsin Department of Natural Resources Fish Hatchery near Madison, Wisconsin.

Calculation of the solubility of aluminum(III) indicated that dissolved aluminum would be below toxic limits for a variety of algae and zooplankton as indicated in the literature. In the laboratory column and jar tests, green algae proliferated on the settled floc after a few days had passed; the persistence of *Cyclops* and *Daphnia* was also noted, indicating their compatibility with the dissolved and suspended materials from the alum treatment.

The concentration of sulfates in the water prior to treatment indicates that sulfate is not limiting the production of sulfides during periods of thermal stratification. The proposed treatment, if all the alum were to be dissolved, would increase the sulfate concentration in the lake by about 10 mg/l. Local precipitation of calcium sulfate is possible in the surface waters of the lake before the sulfate is mixed into more than the top several feet of water, but this should not adversely affect the lake biota.

The long-term effects of alum treatment on benthic organisms were not studied. However, Jernelov and Lundstrom (1969) did toxicological studies on some lake invertebrates in connection with their treatment of a Swedish lake and found no adverse effects.

Given the time and monetary constraints of the project, adequate evaluations of environmental effects, especially long-term effects, of treatment were not possible. The limited studies noted above served merely to insure against large-scale ecologic dislocations. Nevertheless, based on these studies, plus literature surveys, it appeared possible to conduct the alum treatment relatively safely. This conclusion, plus the potential benefits from nutrient removal, justified a field demonstration of the method.

FIELD PROCEDURES

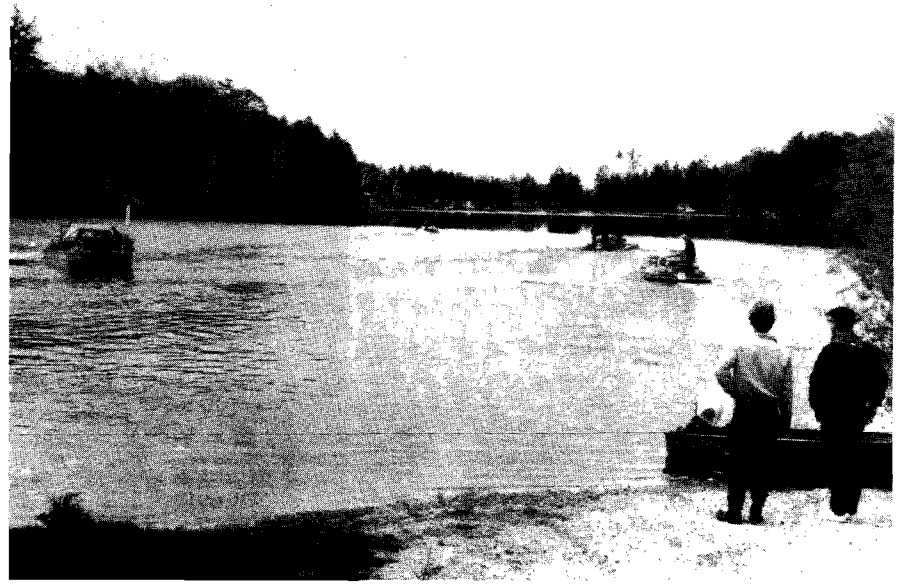
APPLICATION METHODS AND EQUIPMENT

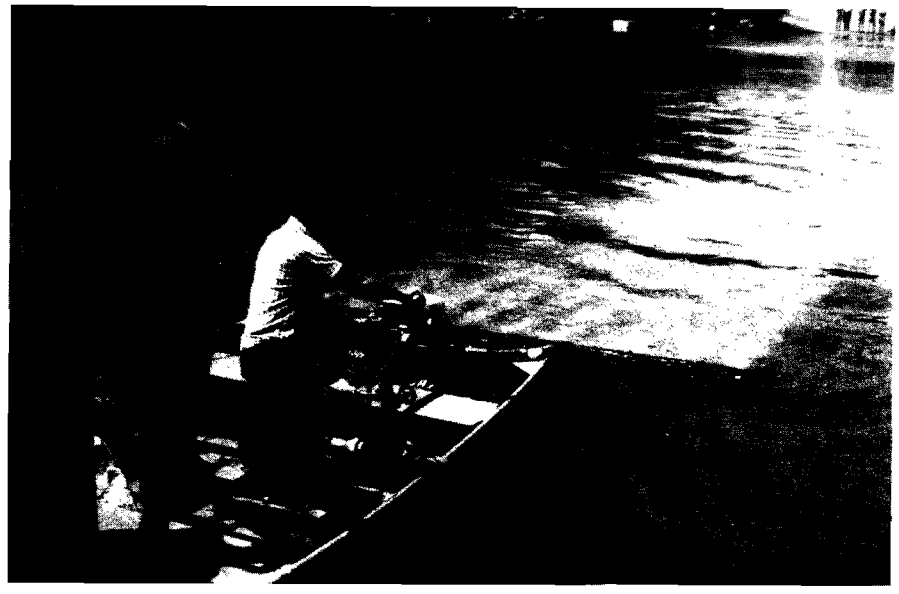
Method of Application. Laboratory tests had determined that flocs of hydrous aluminum oxide (aluminum hydroxide) could remove substantial fractions of dissolved and suspended phosphorus from water. Effective floc formation required addition of an alum slurry rather than the granular material. Good mixing of the slurry into the lake water was necessary. A field trial using alum and fluorescein dye showed that injection of the slurry through a manifold, at about one foot below the water surface, behind a propeller-driven vehicle could produce the desired dispersal.

Description of Equipment. Three similar units for spreading alum were assembled, representing various degrees of stability, application rate, versatility and availability. The equipment consisted basically of slurry tanks, a fresh water supply for filling these tanks, a mixer, an application pump, and a distribution manifold. A detailed description of the units is presented in Appendix A.

To distribute the chemicals, the lake was marked off in 9 plots of about 2.5 acres (1.01 ha) each (Fig. 6). Predetermined amounts of alum were then spread in each area as evenly as possible.

Application and Costs. On May 20, 1970, 22,400 pounds (10.2 metric tons) of alum were distributed in the lake in a period of about 4 hours. A southerly wind of about 10-15 mph (16.1-24.1 kmph) provided surface mixing and dispersion of the chemicals,





Equipment and operation at Horseshoe Lake

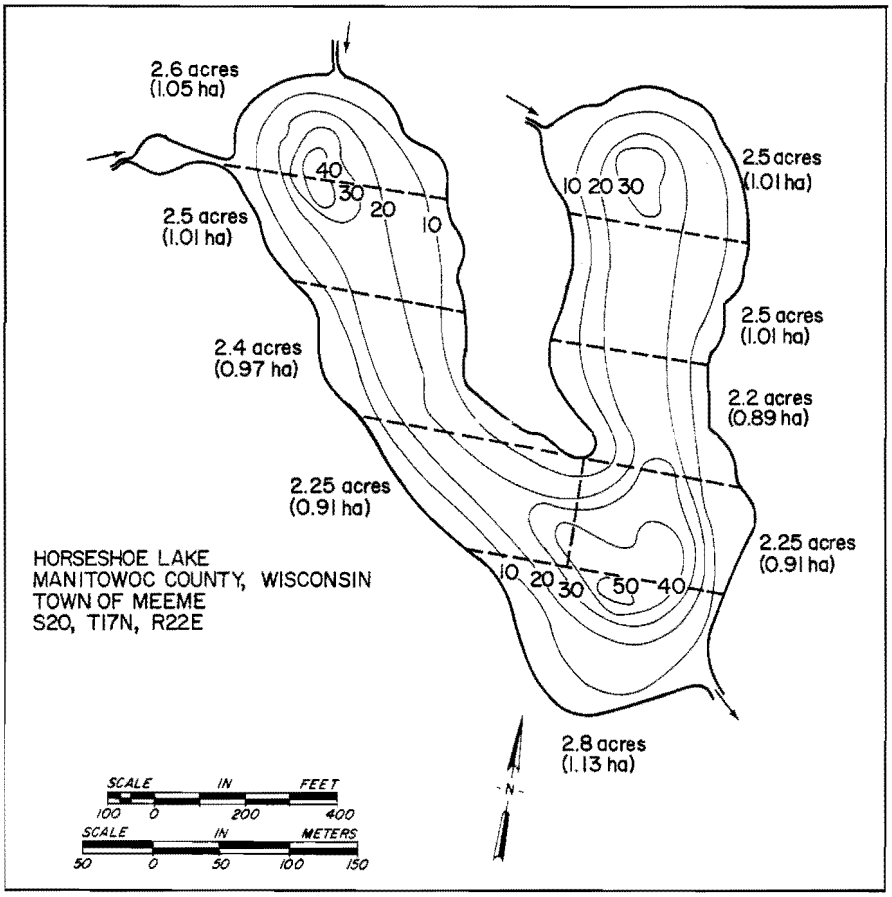


FIGURE 6. *Alum Distribution Zones, Horseshoe Lake.*

and tended to sweep the small amounts of floating floc into the northern ends of the lake. The floc was a dark brown color, as a result of removal of color and particulates from the water. The presence of the floc either as a floating scum or on the bottom in shallow areas was not visible after a few days. A summary of the manpower, equipment, and costs directly associated with the treatment is presented in Appendix B.

DATA COLLECTION

Data Collection. A sampling program was initiated in January, 1970, to gather pretreatment data in order to document the effects of treatment and to provide a basis for comparison with background data from 1966. Stations were established over the three deep areas in the lake. Water samples were collected at 5 foot (1.5 m) intervals along vertical profiles to monitor bulk properties of the water. Temperature, dissolved oxygen, pH, total alkalinity, and transparency (Secchi disc) were measured routinely in the field. Water samples were analyzed in the laboratory for nitrogen and phosphorus species, sulfate and chloride, and several metals (calcium, magnesium, sodium and potassium). Color, conductance, and aluminum determinations were carried out on selected samples. Because analyses showed similar values for samples taken at comparable depths at the three stations, the south basin was selected for monitoring on a regular basis, while sampling at the two other stations was conducted intermittently. In addition to the 1966 data, there were six sampling dates prior to treatment, two series on the day of treatment, and 30 dates during the next 22 months after treatment.

Sampling for biological examination was conducted periodically. Samples were collected either with a towed plankton sampler or by filtering grab samples through bolting cloth or membrane filters.

Analytical Methods. Water analyses for most parameters were conducted according to methods described in Standard Methods (Amer. Pub. Health Assoc. et al, 1965), with the following exceptions:

(1) Some pH measurements were done in the field using a color comparator.

(2) Color was determined using glass comparison discs calibrated against chloroplatinate standard solutions. Samples were passed through 0.45 μm membrane filters, and the pH was not adjusted.

(3) Calcium, magnesium, sodium, potassium and aluminum were determined by atomic absorption (FWPCA, 1969).

(4) Phosphorus determinations for the laboratory studies were made using the Murphy-Riley method described by Jankovic, Mitchell and Buzzell (1967).

RESULTS AND DISCUSSION

PHOSPHORUS

Plots of the total phosphorus concentration in the epilimnetic and hypolimnetic waters for 1966, 1970, 1971, and 1972 are shown in Figures 7 and 8. The 1966 data reflect qualitative phosphorus changes typical of a thermally stratified, eutrophic lake. That is, the increase in hypolimnetic total phosphorus and the concurrent decrease in epilimnetic total phosphorus commence soon after the onset of thermal stratification. Some decrease in phosphorus levels from 1966 to 1970 would be expected, since a source of nutrient enrichment had been stemmed. The changes coincident with treatment, however, are substantial compared to pro-rated decreases over the previous 4-year period.

A comparison of the 1966 and 1970 epilimnetic series shows similar qualitative trends, but the 1970 values are generally lower than those of 1966. However, the **hypolimnetic** values for the two years show different trends. The 1966 hypolimnetic curve displays a typical increase in phosphorus concentration, but the 1970 phosphorus values remain relatively stable and consistently lower throughout the summer stratification period. It would appear that as a result of treatment:

(1) **Epilimnetic** total phosphorus values following treatment in May, 1970, have been consistently lower than those for a comparable period

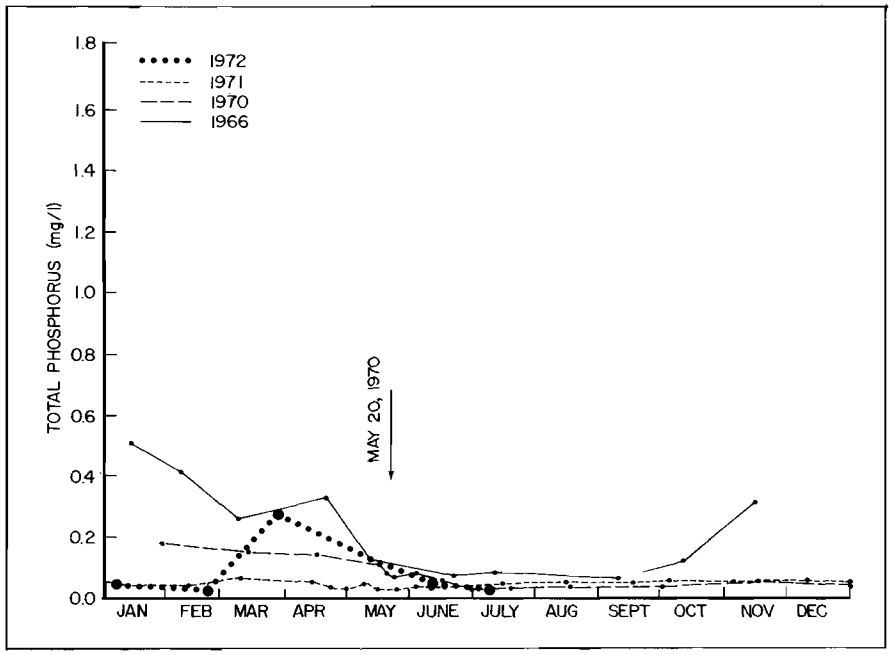


FIGURE 7. *Epilimnetic Total Phosphorus Concentrations, Horseshoe Lake.*

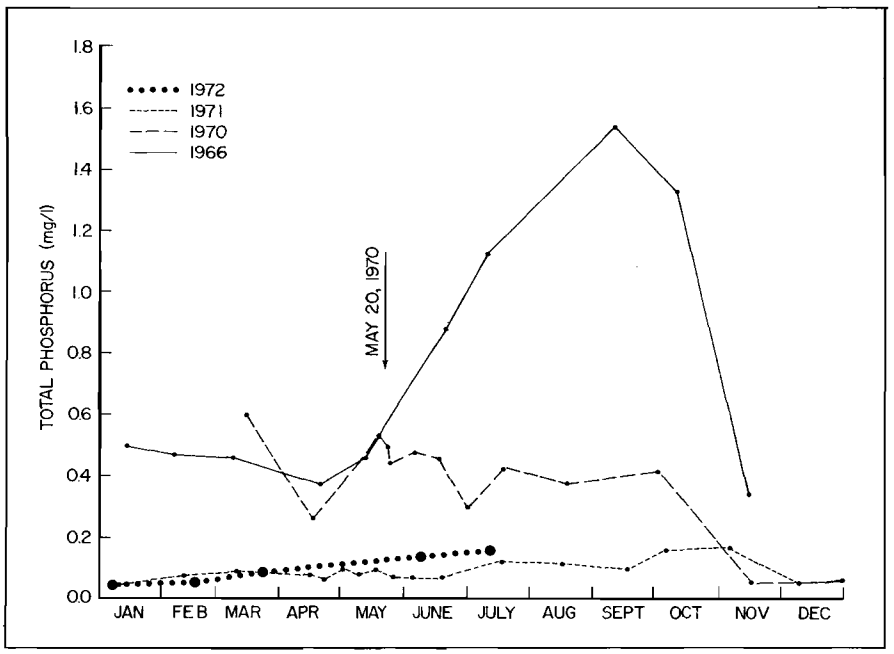


FIGURE 8. *Hypolimnetic Total Phosphorus Concentrations, Horseshoe Lake.*

(May-November) in 1966; 1970 (0.02-0.06 mg/l); 1966 (0.05-0.10 mg/l).

(2) **Hypolimnetic** total phosphorus values were also consistently lower than for the same period (May-November) in 1966; 1970 (0.4-0.5); 1966 (0.5-1.5 mg/l). Moreover, no increase in hypolimnetic total phosphorus values took place during the summer stratifications following alum treatment; such an increase had occurred during the summer of 1966, and is typical of stratified eutrophic lakes. The atypical behavior (for eutrophic lakes) of phosphorus in the hypolimnion may have been the result of a decrease in particulate matter settling down from the epilimnion subsequent to treatment and/or an influence of the treatment on phosphorus release from bottom sediments.

(3) The total phosphorus concentration present in the entire lake at fall turnover in 1970 (0.04 mg/l) was substantially less than that at spring turnover (0.15 mg/l), or for similar periods in 1966 (0.3-0.4 mg/l).

Low levels of total phosphorus were the rule during 1971 and 1972 (Figs. 7 and 8). Total phosphorus concentrations in the epilimnion ranged from 0.02 mg/l to 0.32 mg/l; in the hypolimnion from 0.04 to 0.31 mg/l. (The high total phosphorus concentration in March 1972 corresponded to high nitrogen levels and high potassium levels in the surface waters as well as in the inlet stream, and were apparently related to snowmelt and runoff from the basin.) While the improvement of dissolved oxygen conditions may have contributed to the maintenance of lower phosphorus concentrations, there was again no large increase of phosphorus in the anaerobic hypolimnion during the summer stratification, 1971. It is possible that the aluminum-based floc acts at the mud-water interface to retard the passage of phosphorus from the sediment to the water. The complete knowledge of this process would have a determining role in the feasibility of the renovation scheme, as it would show whether longer range benefits may be expected to accrue from aluminum ion application. Perusal of the data for weighted average total P in the lake (Fig. 9) shows a decrease following treatment, and no substantial return to pretreatment levels. Demonstration Project-funded studies on suppression of phosphorus mobility at the sediment-water interface by hydrous aluminum oxides (using intact lake cores under anoxic conditions) are in progress; they have shown no increase in dissolved phosphorus concentrations in the water column several months after treatment (Syers and Browman, 1972).

Estimates based on water analyses indicate that the treatment of Horseshoe Lake precipitated from 10 to 15 pounds (4.5-6.8 kg) of phosphorus to the bottom of the lake within a few days. Based on the spring-fall turnover (1970) total phosphorus concentration differences, a net decrease in phosphorus of approximately 110 pounds (50 kg) had occurred over the summer. If this were to be the extent of the benefits it is doubtful that the technique would prove to be economically practical. Further laboratory and field investigations are attempting to determine if a direct relationship exists between the aluminum treatment and the decrease of phosphorus in the anaerobic hypolimnion which has lasted for nearly two years after treatment.

TRANSPARENCY

The transparency (Secchi disc read-

ing) data are presented in Figure 10. The transparency data for 1966 and 1970 fall in the same range (2-15 feet, 0.6-4.6 m), but the 1970 measurements show an increase in transparency for longer periods of the summer.

Immediately following treatment, a marked increase in Secchi disc reading was noted. Heavy rainfall and attendant runoff shortly after treatment (3.31 inches during May 22-24 and 1.44 inches on May 30-31) resulted in the low transparencies recorded for early June. However, Secchi readings improved throughout the remainder of the summer. Increased transparency was accompanied by low planktonic algal populations (less than 60 organisms/liter). Residents on Horseshoe Lake claimed that 1970 had been the best "water quality" year in a long time, and no complaints of planktonic algal nuisances (or fish kills) were reported. At the time of treatment, suspended solids were about 1.2 mg/l. The level decreased to 0.6 mg/l in mid-July and to about 0.1 mg/l in August, which is in general accord with transparency measurements.

The use of transparency measurements as an indicator of improvements may be misleading. Copper sulfate was applied to littoral zone areas during 1970 and 1971 for control of *Chara* and other filamentous algae (Fig. 10). In 1971 the increase in Secchi reading from about 6 feet to near 12 feet corresponded to the time of copper treatment. In 1970, the Secchi reading had been increasing prior to the copper application, but the treatment may have prolonged the higher transparency period. The 1966 treatment, however, did not result in a long-term increase in clarity, even though nearly twice as much copper had been applied.

COLOR

Color values for epilimnetic and hypolimnetic waters in 1970 showed a short-term decrease as a result of alum treatment (Fig. 11). The effect on the hypolimnetic waters was less dramatic than in the surface waters where color was reduced from 20-25 units to less than 10 units for a period of several days. No color measurements are available from past data from a comparison. The color increase around June 3 seems to have been related to the heavy rains that occurred after treatment. No lasting effects were noted, as color approached pretreatment levels by the end of 1970.

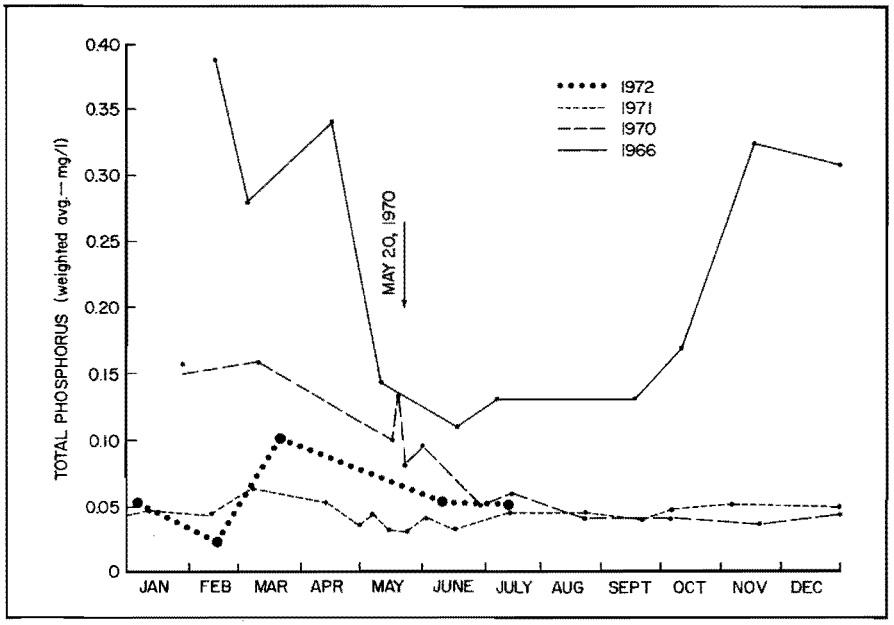


FIGURE 9. *Weighted Average Total Phosphorus, Horseshoe Lake.*

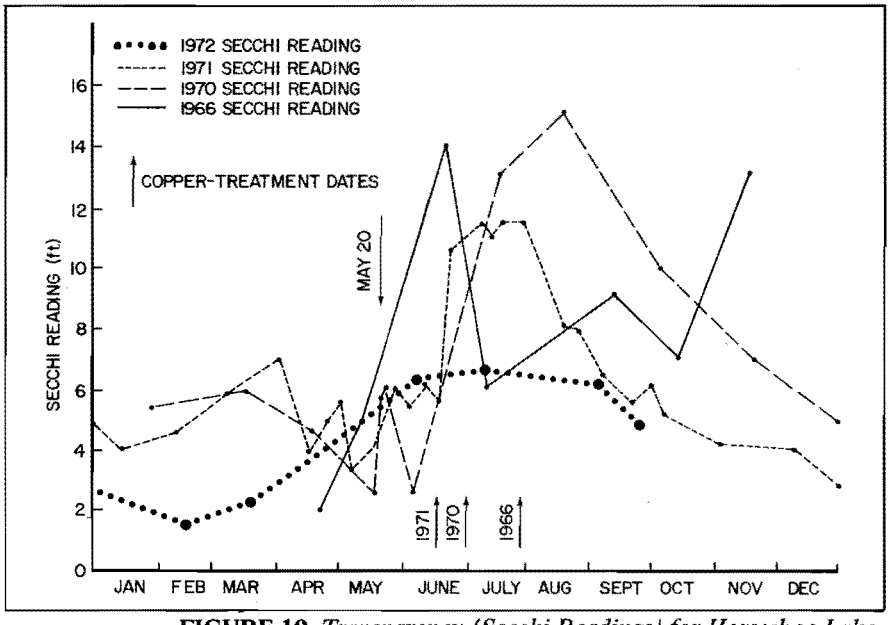


FIGURE 10. *Transparency (Secchi Readings) for Horseshoe Lake, 1966, 1970 and 1971.*

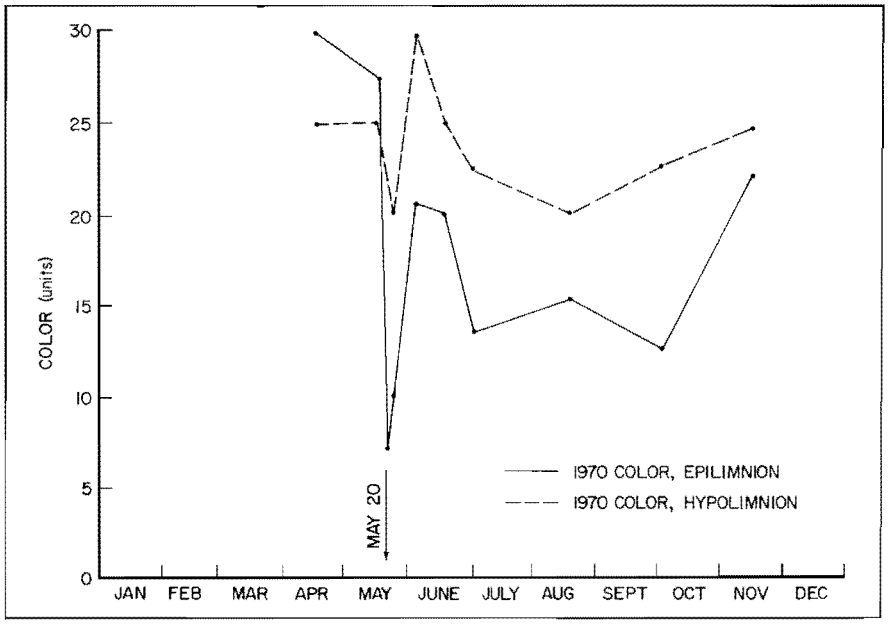


FIGURE 11. *True Color in Horseshoe Lake Waters.*

NITROGEN

Four species of nitrogen are routinely determined--nitrite, nitrate, ammonia, and organic nitrogen. All of the nitrogen forms showed increases in concentration during the spring of 1971 whereas the values for 1966 and 1970 showed a steady decrease during both years. Considering these as total nitrogen, weighted average concentrations were calculated and the results are presented in Figure 12. The 1971 data show uncharacteristically high values in March, April, and May, which are due primarily to higher nitrate values. There is a steady decline during the summer, 1971, but it is not until September that the level of total nitrogen reaches those of 1966 and 1970. As anticipated, the aluminum treatment had no apparent positive effect on limiting total nitrogen content of the water.

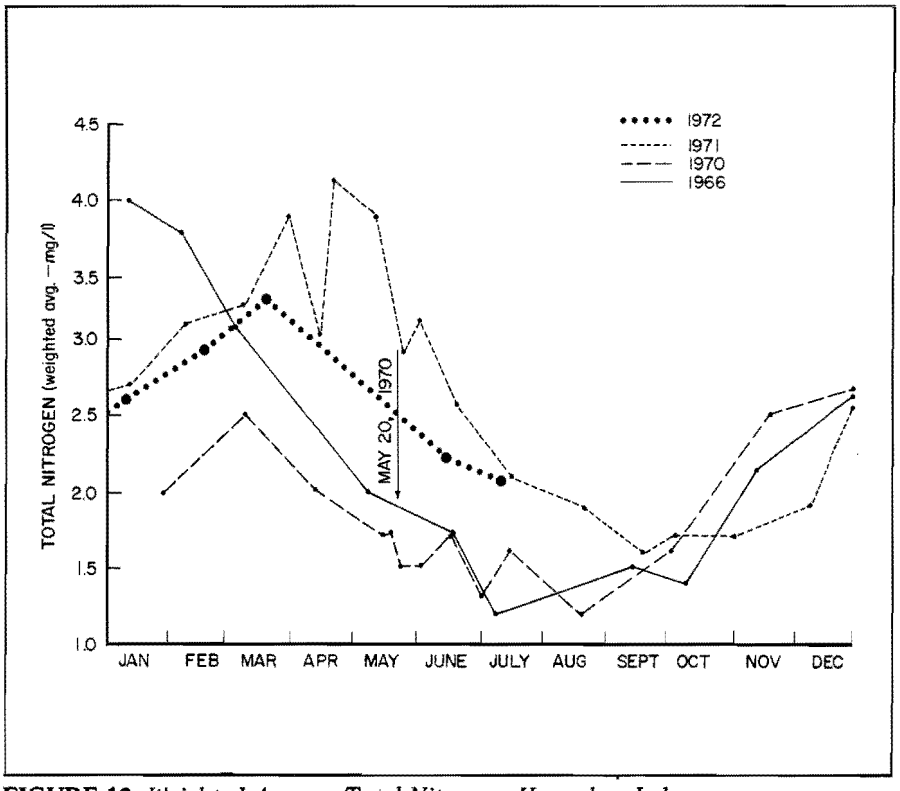


FIGURE 12. *Weighted Average Total Nitrogen, Horseshoe Lake.*

DISSOLVED OXYGEN

The 1970 dissolved oxygen (D.O.) data show that the depth to the regions of depleted oxygen increased from about 15 feet (4.6 m) at treatment time (May 20, 1970) to about 20 feet (6.1 m) as the summer progressed (Fig. 13). This increased dissolved oxygen excursion was due to a combination of the increased transparency of the water and the deepening of the thermocline (Fig. 14). Dissolved oxygen was essentially depleted throughout the lake during the pretreatment winter of 1969-70, as had been common in previous years.

In contrast, D.O. concentrations during the 1970-71 winter and again in 1971-72 have been adequate to support a sport fishery. The 1971 summer D.O.'s also showed an improvement over 1970.

Snow cover during the three recent winters was heavy, and was comparable to previous winters in which winterkill had been observed.

BOTTOM FAUNA

Chaoborus larvae were observed near the sediment-water interface on cores taken in January, 1971.

A more extensive survey of the benthic fauna of Horseshoe Lake was done in April, 1971. Four Ekman dredge samples were collected through the ice at each of the five points in the lake indicated in Figure 15. Organisms were first isolated by retention on a 60-mesh sieve, preserved in 70 percent ethanol, and sorted in the laboratory. All insects were counted as were all leeches, mites, snails, and clams. Chironomidae larvae less than 5 mm long, Ostracoda, Copepoda, and Cladocera were enumerated by a subsampling technique. The results are shown in Table 8. The consistent presence of *Chaoborus* suggests that it experienced no extensive damage as a result of the treatment. The fauna of Horseshoe Lake is not atypical of that found in deep, eutrophic lakes which experience hypolimnetic oxygen depletion.

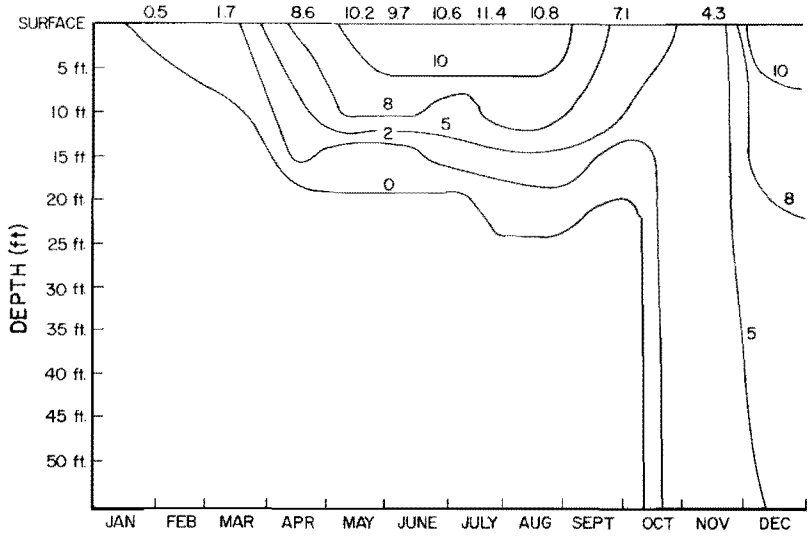
OTHER PARAMETERS

Analyses were made on selected water samples for aluminum and sulfate to observe alum distribution patterns and the mixing of ionic species in the lake. The precision and frequency of these data do not permit extensive interpretation. Aluminum concentrations in the epilimnion were all less than 1 mg/l before treatment, and returned to this low range within six days thereafter.

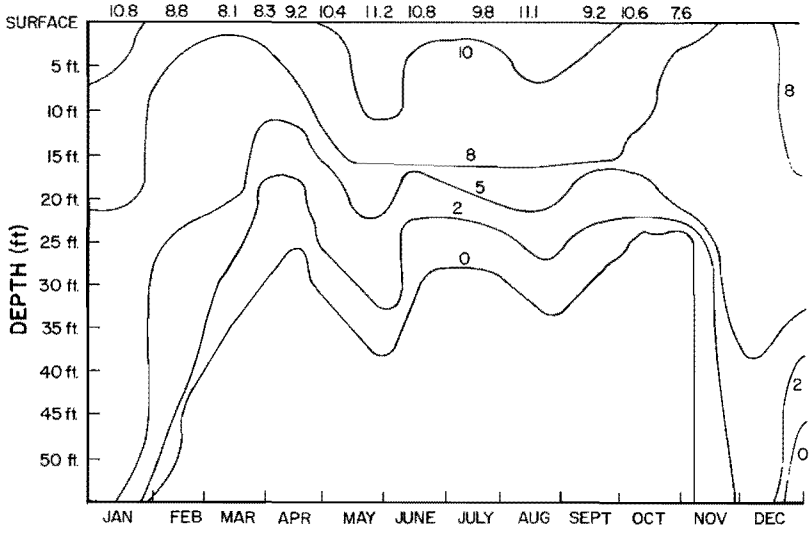
Analyses for calcium, magnesium, sodium and potassium were performed to provide a more complete characterization of Horseshoe Lake waters. No significant changes were noted. The short-lived pH decrease in the surface waters of the lake (about 0.5 pH units) was comparable to decreases observed in laboratory jar testing.

SEDIMENTS

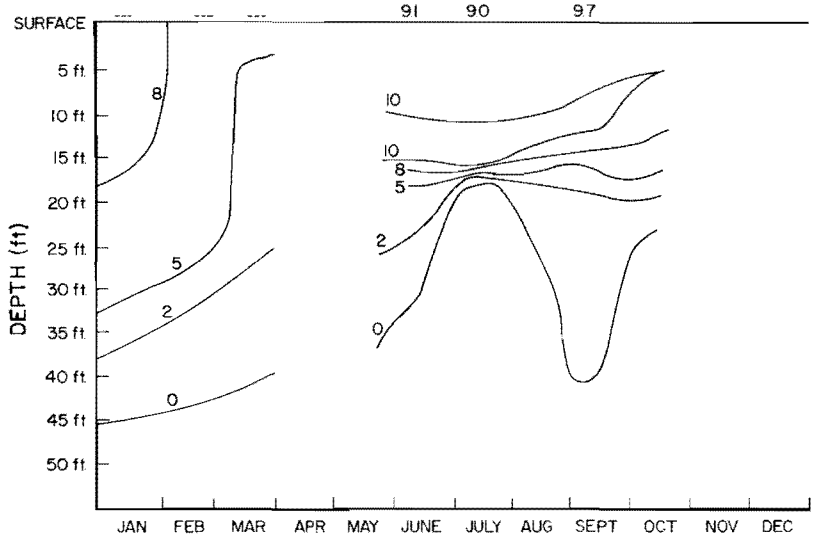
Duplicate sediment cores were taken from the deep area of the lake in January 1971 for chemical characterization. No visual evidence of the aluminum-based floc from treatment in 1970 could be detected. The analytical data shown in Table 9 depict a calcareous sediment containing moderate amounts of organic materials. The analyses on similar sections of the two cores all agreed within 10 percent. The relatively higher inorganic P (1N acid-leachable) at the sediment surface (0-5 cm) may reflect the results of treatment, but no increase is noted in the Bray P_2 results which should detect aluminum-bound P. The sediment profile did show evidence of copper treatments which have been applied over the past years. The aluminum content of the sediments is high and variable enough to preclude observing an increase in aluminum in the upper parts of the sediment column as a consequence of treatment. Calculation of the amounts of aluminum and phosphorus which would be necessary to show substantial increases in the analytical values for the surface sediments indicate that it is unlikely that such changes would be observed, because of the amounts of material applied, and the length of the core sections analyzed.



1970



1971



1972

FIGURE 13. *Dissolved Oxygen in Horseshoe Lake*

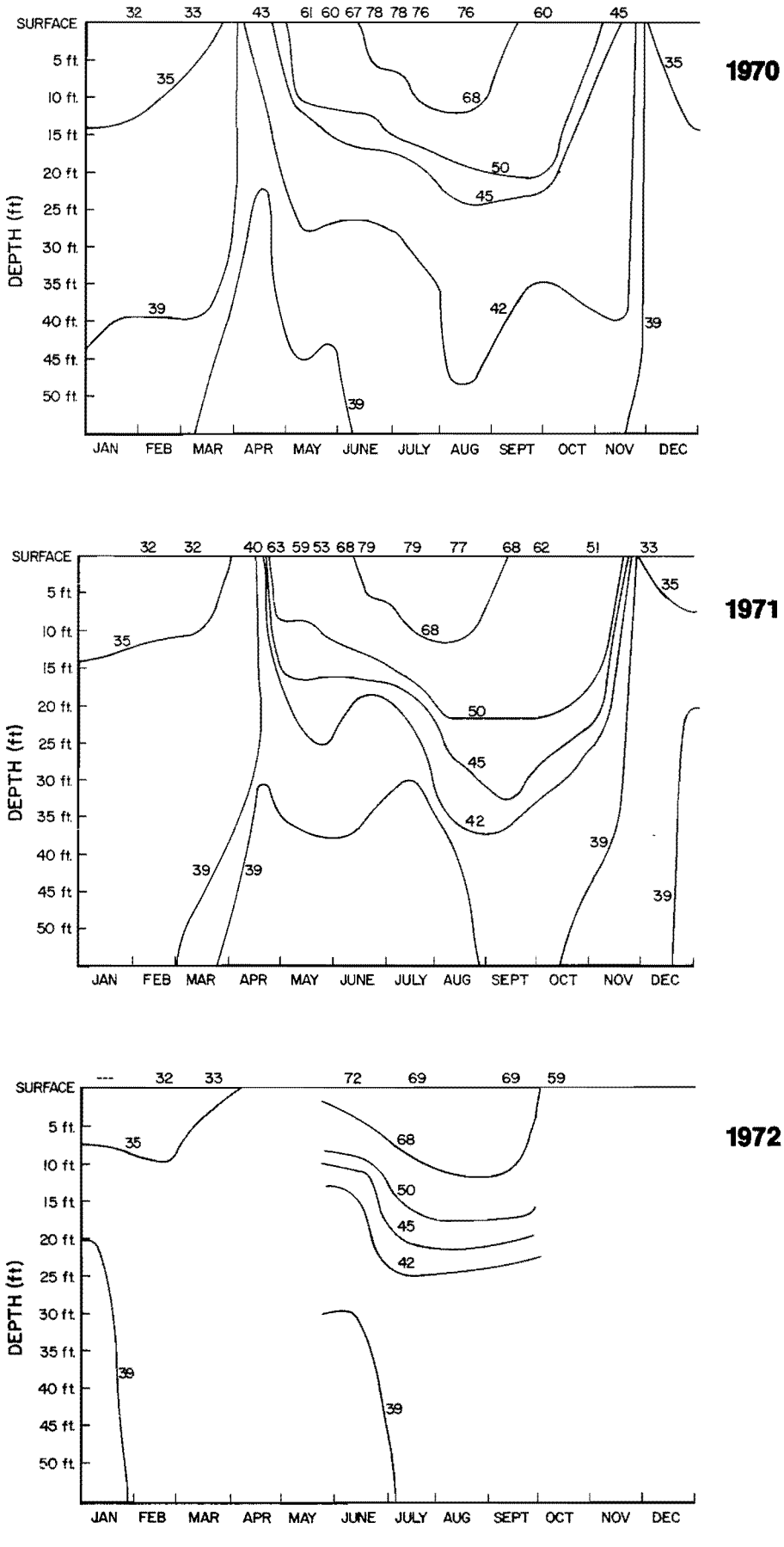


FIGURE 14. *Temperature in Horseshoe Lake*

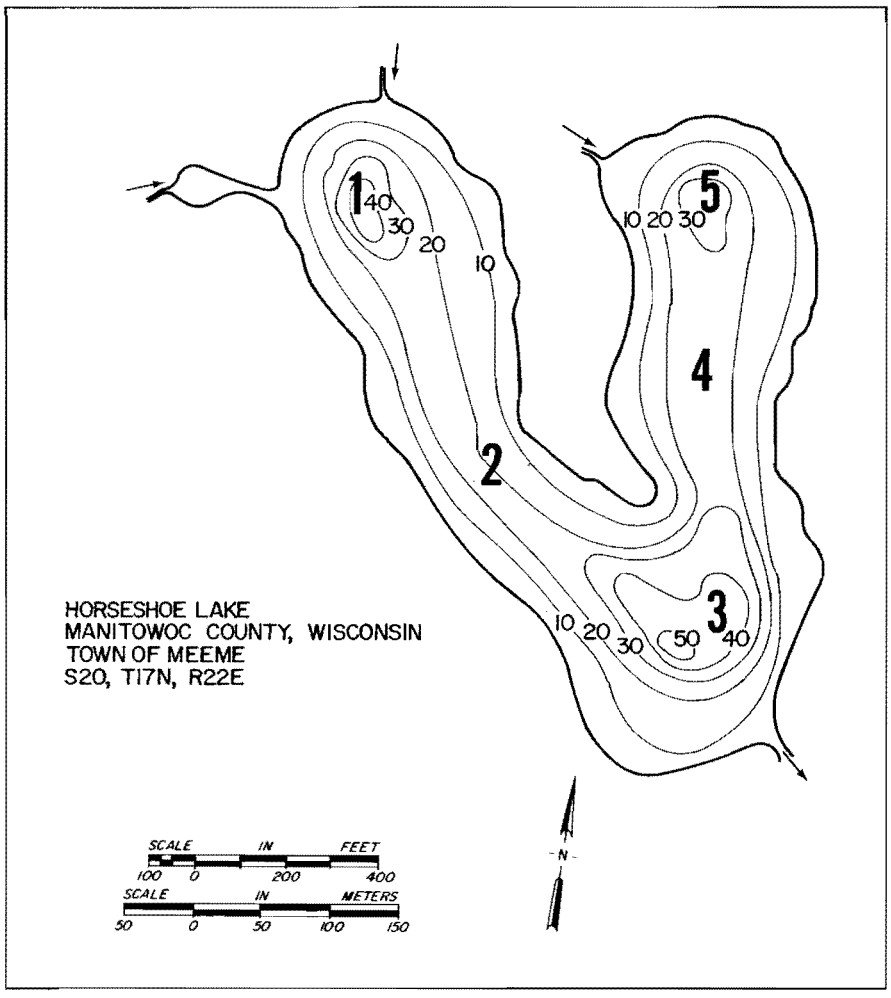


FIGURE 15. *Benthic Fauna Survey Stations, 1971.*

CONCLUSIONS

Horseshoe Lake was treated on May 20, 1970, by distributing 11¼ tons (10,200 kg) of slurried alum in the top 2 feet (0.6 m) of water. The objective of the treatment was to reduce the amount of phosphorus available to plants in the lake waters, and thereby limit the propagation of nuisance planktonic algal growths. The results of treatment include:

(1) A decrease in total phosphorus in the lake during the summer following treatment.

(2) No large increase in total phosphorus in the hypolimnion during the following two summer stratifications.

(3) Some increase in the transparency of the water during the summer following treatment.

(4) A short-term decrease in color.

(5) An absence of the nuisance planktonic algal blooms that had been common in previous years.

(6) Marked improvement in dissolved oxygen conditions, particularly during the following winters.

(7) No observations of adverse ecological consequences.

TABLE 8. Benthic Fauna Survey, Horseshoe Lake, 1971 (Numbers of benthos per square foot)

	Sampling Site				
	1	2	3	4	5
Ostracoda	240	0	0	0	0
Chironomus larvae 6–8 mm	0	0	0	1	0
15–17 mm	0	0	0	1	0
Chaoborus larvae	61	228	576	54	184

Numbers per square foot x 10.76 = numbers per square meter.

FUTURE PROGRAMS

Upon termination of the Inland Lake Demonstration Project, the water-quality monitoring program at Horseshoe Lake will be continued by the Wisconsin Department of Natural Resources to provide data on the longer-term effects of alum treatment. Of particular interest is permanence of the treatment benefits, especially with respect to phosphorus release from sediments under anoxic conditions.

We hope that the generally positive results obtained in this demonstration project will stimulate longer-term and more thorough research evaluations of chemical nutrient inactivation as a viable renovation technique for certain lakes impaired by accelerated eutrophication.

TABLE 9. Sediment Core Characteristics, Horseshoe Lake, January, 1971

Depth in Core cm	Solids %	NH_4^+–N mg/g	Total N %	Organic Carbon %	Inorganic P mg/g	Bray P_2 µg/g	Ca %	Cu µg/g	Aluminum mg/g
0–5	8.9	0.30	1.3	11.8	0.66	6	13.1	114	6.9
5–10	15.7	0.30	1.0	10.4	0.39	8	14.1	27	7.9
10–15	18.8	0.34	0.9	9.1	0.43	8	10.7	30	11.9
15–20	20.8	0.22	0.8	8.6	0.46	6	13.6	25	9.4
20–25	15.9	0.14	1.0	10.6	0.43	8	12.0	22	9.1
30–35	17.8	0.18	1.2	12.7	0.45	3	13.6	25	7.1
45–50	11.2	0.26	1.9	18.1	0.48	4	9.4	31	3.5
60–65	12.3	0.18	1.8	17.3	0.67	4	11.8	31	3.1

APPENDIX A: Description of Equipment

DESCRIPTION OF EQUIPMENT

The smallest unit was put into a 16-foot (4.88 m) aluminum workboat powered by an 18-hp outboard motor. A slurry tank (55-gallon (208 liters) drum) was mounted on decking about mid-ships. Two 3-hp gasoline-driven centrifugal pumps (1½ inch (3.81 cm) x 2 inch (5.08 cm)) were used; one for filling and mixing the slurry tank, the other for pumping the slurry from the tank into the lake through a 1½ inch (3.81 cm) x 10 foot (3.05 m) long plastic pipe manifold (perforated with 5/16 inch (7.94 mm) diameter holes at 1 foot (30.4 cm) intervals). The alum was slurried and applied on a batch basis at a rate of about 700 pounds (317 kg) per hour by two men. This unit was particularly useful for treating shallow areas and places where good maneuverability was required. The equipment is readily available and easy to assemble, but the application rate per man-hour is comparatively low.

The second unit consisted of two 200-gallon (758 l) stock watering tanks, mounted on a 10-foot (3.1 m) by 20-foot (6.1 m) barge (4-ton (3630 kg) load capacity). The barge was powered by an 18-hp outboard motor. The pumping and spreading apparatus were similar to that used on the workboat. Three men could spread about 2,500 pounds (1135 kg) per hour.

The third, an all-electric unit, was aboard a DUKW-353 amphibious, 2½-ton truck (U.S. Army Duck on loan from the University of Wisconsin Water Chemistry Program). Power was supplied to the freshwater and spreading pumps and the tank mixers by a portable, 4,000-watt generator. Three 55-gallon (208 liter) drums were joined with 2-inch (5.08 cm) pipe and quick-opening valves, so that treatment could proceed on a continuous basis. The pumping rates were adjusted to yield a mixing residence time of about 1½ minutes to ensure effective solution/suspension of the alum. A 12-foot (3.66 m) wide spreader manifold of perforated 1½ inch (3.81 cm) galvanized iron pipe was used to distribute the slurry. This unit was the most stable and easiest to operate, but least maneuverable. It could only operate in water depths exceeding 5 feet (1.5 m); moreover, a good landing is required in order to launch this vehicle. The DUKW-353 unit was operated by three men and could spread about 3,000 pounds (1360 kg) of alum per hour. Addition of another slurry tank and mixer is possible which would increase the output per man-hour. Sufficient power is available so that a larger (wider and/or deeper) manifold could be used, if necessary.

APPENDIX B: Summary of Manpower, Basic Equipment and Costs

	Item	Costs*
Sampling**	8 man-hours per trip @ $5.00/hour	$ 40.00
	270 miles round trip @ $3.00 day + $0.6/mi.	$ 19.20
Analyses**	12 samples per trip @ $30/sample	$ 360.00
Staff	1 professional	$13,000.00
	Overhead	$ 7,300.00
Chemicals	12 tons alum @ $60/ton	$ 720.00
	Delivery to site	$ 180.00
Labor for treatment	12 man days @ $40	$ 480.00
	+ expenses	$ 100.00
Equipment list	2–18 ft. workboats 2–10 ft. x 20 ft. barges 4–outboard motors, 18-25 hp 1–amphibious truck, 2½ ton, DUKW-353 4–gasoline driven pumps 1–4,000 watt generator 2–electric pumps 3–electric mixers 4–55 gallon slurry tanks 2–200 gallon slurry tanks Piping, valves, hose, plastic tubing, marker flags, gasoline, plastic tarp, rope, dust masks	essentially all equipment was on loan

*Many of the costs associated with this treatment are entirely dependent on local salary levels, distances to site, sampling plan, magnitude of treatment, and local availability of equipment. In essence, treatment costs must be estimated for a specified situation.

**A total of 38 sampling runs is included in this report, which would yield a total cost of about $15,900 for sampling and analysis–not including the 1966 data.

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